

FINAL REPORT

Cyclic Dinitroureas As Self-Remediating Munition Charges

SERDP Project WP-1624

FEBRUARY 2009

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REPORT DOCUMENTATION PAGE				<i>Form Approved</i> <i>OMB No. 0704-0188</i>							
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1. REPORT DATE (DD-MM-YYYY) 26-02-2009		2. REPORT TYPE Final		3. DATES COVERED (From - To) Feb 2008–Feb 2009							
4. TITLE AND SUBTITLE Cyclic Dinitroureas As Self-Remediating Munition Charges				5a. CONTRACT NUMBER							
				5b. GRANT NUMBER							
				5c. PROGRAM ELEMENT NUMBER 603716D							
6. AUTHOR(S) Chapman, Robert D. Quintana, Roxanne L. Baldwin, Lawrence C. Hollins, Richard A.				5d. PROJECT NUMBER WP-1624							
				5e. TASK NUMBER							
				5f. WORK UNIT NUMBER							
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Chemistry Branch (Code 4L4200D) Naval Air Warfare Center Weapons Division 1900 N. Knox Rd. Stop 6303 China Lake, CA 93555-6106				8. PERFORMING ORGANIZATION REPORT NUMBER							
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) SERDP & ESTCP Program Offices 901 North Stuart Street, Suite 303 Arlington, VA 22203-1853				10. SPONSOR/MONITOR'S ACRONYM(S) SERDP							
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)							
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited											
13. SUPPLEMENTARY NOTES											
14. ABSTRACT <p>As a potential solution to persistent environmental problems posed by conventional nitramines in unexploded ordnance (UXO), we investigated certain cyclic N,N'-dinitrourea derivatives: tetranitroglycoluril (TNGU) and hexanitrohexaazatricyclododecanedione (HHTDD), comparable in performance to HMX and CL-20. A property these compounds have in common that has kept them from widespread adoption by most weapons systems is a property that makes them attractive in specific systems that are susceptible to causing environmental problems as UXO: they are more hydrolytically reactive than simple alicyclic nitramines such as RDX. We quantified these ingredients' susceptibility to environmental hydrolysis in order to demonstrate that they show acceptable stability for processing into munitions but also suitable reactivity with environmental elements that they would undergo sufficiently rapid "spontaneous" (environmentally adventitious) degradation as to constitute "self-remediation." The kinetics of ingredient degradation were determined under several environmental conditions. TNGU and HHTDD were seen to be stable enough in humidity-controlled air to manufacture and process; in moist soil and even in humid air, however, they degrade over hours to a very few days, and kinetic analysis shows the hydrolysis to be autocatalytic in mechanism. It is concluded that this class of ingredients does offer suitable replacements for conventional nitramines in venues that are susceptible to UXO formation.</p>											
15. SUBJECT TERMS Tetranitroglycoluril; hexanitrohexaazatricyclododecanedione; TNGU; HHTDD; hydrolysis; UXO											
16. SECURITY CLASSIFICATION OF: <table border="1" style="width: 100%; border-collapse: collapse; font-size: 0.8em;"> <tr> <td style="width: 33%;">a. REPORT</td> <td style="width: 33%;">b. ABSTRACT</td> <td style="width: 33%;">c. THIS PAGE</td> </tr> <tr> <td>Unclassified</td> <td>Unclassified</td> <td>Unclassified</td> </tr> </table>			a. REPORT	b. ABSTRACT	c. THIS PAGE	Unclassified	Unclassified	Unclassified	17. LIMITATION OF ABSTRACT Unclassified Unlimited		18. NUMBER OF PAGES 23
a. REPORT	b. ABSTRACT	c. THIS PAGE									
Unclassified	Unclassified	Unclassified									
			19a. NAME OF RESPONSIBLE PERSON Robert D. Chapman								
			19b. TELEPHONE NUMBER (Include area code) 760-939-1663								

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Table of Contents

List of Acronyms	ii
List of Figures	ii
Acknowledgements	ii
Executive Summary	1
Objective	2
Background	2
Materials and Methods.....	6
Results and Accomplishments	10
Conclusions.....	18
Appendix. List of Technical Publications.....	20

List of Acronyms

AGFI	Adjusted goodness of fit index
BLU	Bomb Live Unit
CBU	Cluster Bomb Unit
CL-20	Hexanitrohexaazaisowurtzitane
HHTDD	Hexanitrohexaazatricyclododecanedione
HPLC	High-performance liquid chromatography
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
NAWCWD	Naval Air Warfare Center Weapons Division
NMR	Nuclear magnetic resonance
PBXN	Plastic Bonded eXplosive (Navy)
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
RH	Relative Humidity
SEED	SERDP Exploratory Development
TNGU	Tetranitroglycoluril
UXO	Unexploded ordnance

List of Figures

Figure 1. Synthetic routes reported to prepare HHTDD	5
Figure 2. Suggested hydrolysis mechanism of HHTDD	6
Figure 3. Chosen preparation of HHTDD.....	7
Figure 4. ¹ H NMR spectrum obtained from a typical sample extract.....	8
Figure 5. Degradation of HHTDD and TNGU in humid air (85% RH)	11
Figure 6. Degradation of HHTDD and TNGU in 1:4 water:soil	13
Figure 7. Degradation of HHTDD and TNGU in dry air (28% RH).....	15
Figure 8. Degradation of HHTDD and TNGU in contact with “dry” soil (air at 28% RH)	17

List of Tables

Table 1. Explosive performance parameters of cyclic dinitroureas vs. nitramines	4
Table 2. Humid air (85% RH) hydrolysis of HHTDD.....	11
Table 3. Humid air (85% RH) hydrolysis of TNGU	12
Table 4. Moist soil hydrolysis of HHTDD and of TNGU	12
Table 5. Dry air (28% RH) hydrolysis of HHTDD	14
Table 6. Dry air (28% RH) hydrolysis of TNGU	14
Table 7. Dry soil hydrolysis of HHTDD (air@28% RH).....	16
Table 8. Dry soil hydrolysis of TNGU (air@28% RH).....	16

Acknowledgements

In addition to the Principal Investigator, Roxanne L. Quintana, Dr. Lawrence C. Baldwin, and Dr. Richard A. Hollins (all of the Chemistry Branch, Research Division, Research Department, NAWCWD) carried out the work described in this report. This research was supported fully by the Department of Defense, through the Strategic Environmental Research and Development Program (SERDP).

Executive Summary

Submunition fills in weapons such as BLU-97/B bomblets pose safety and/or environmental hazards if they end up as UXO due to dudding. Incomplete (low-order) detonation of fills in larger munitions that employ nitramine-based charges could also lead to environmental and safety problems as UXO. A typical submunition fill employing RDX as the main explosive charge could exhibit significant deleterious environmental effects on water supplies. RDX also has high to moderate mobility in soil, and its natural (aerobic) biodegradation is very slow.

As a potential solution to persistent environmental problems posed by such ingredients in UXO, we investigated a class of explosive energetic ingredient that has received some development (predominantly in other countries) over the last couple of decades: cyclic *N,N'*-dinitrourea derivatives. Specific examples investigated included tetranitroglycoluril (TNGU or Sorguyl) and hexanitrohexaazatricyclododecanedione (HHTDD). A property these compounds have in common that has kept them from widespread adoption by most weapons systems is a property that makes them attractive in specific systems that are susceptible to causing environmental problems as UXO: they are significantly more hydrolytically reactive than simple alicyclic nitramines such as RDX. With processing problems technologically solved, these ingredients would offer attractive performance advantages, particularly in the case of HHTDD, which is recognized to be the most powerful easily accessible explosive compound, surpassing even CL-20 in explosive performance. (TNGU is comparable in performance to HMX.)

We quantified these ingredients' susceptibility to environmental hydrolysis in order to demonstrate that one or more of them shows acceptable stability for processing into munitions but also suitable reactivity with environmental elements that they would undergo sufficiently rapid "spontaneous" (environmentally adventitious) degradation as to constitute "self-remediation." The kinetics of ingredient degradation were determined under several environmental conditions (all at ambient 23 °C): humidity-controlled laboratory air (~28% RH), artificially humid air (85% RH), moist topsoil (Horizon A with 20 wt% water), and dry (ambient) topsoil. Sample analysis was performed by NMR spectrometry following an extraction involving ultrasonic dissolution of energetics into acetonitrile-*d*₃, allowing determination of environmental lifetimes of the ingredients under various test conditions.

TNGU and HHTDD were seen to be stable enough in humidity-controlled air to produce and process, with no significant change occurring over a few days. In humid air, however, they degrade over a very few days, and kinetic analysis shows the hydrolysis to be autocatalytic in mechanism. At 85% RH, the time required to degrade by 50% (*t*₅₀) is 0.95 day for HHTDD and 3.67 days for TNGU. In moist topsoil, HHTDD is fully hydrolyzed in <19 hours, and TNGU is 99.6% hydrolyzed in 26 hours. Long-term analyses of hydrolysis over several months in dry (ambient laboratory) air as well as in intimate contact with "dry" (ambient) topsoil show extrapolations to 50% degradation (*t*₅₀) on the order of 6–9 months for both ingredients. Thus, the efficiency of these ingredients' "self-remediation" is highly dependent on ambient humidity or access to any source of water. It is concluded, therefore, that this class of ingredients—particularly the chosen examples, HHTDD and TNGU—does offer suitable replacements for conventional nitramines in venues that are susceptible to UXO formation.

This SEED project constituted a feasibility demonstration that certain examples of cyclic dinitroureas are potentially attractive "self-remediating" munitions ingredients. Further process development would be needed in order to develop them as replacements for current problematic formulations.

Objective

SERDP Statement of Need WPSON-08-04 called for technical approaches to reduce the safety and environmental hazards posed by unexploded ordnance (UXO) resulting from munition failures in the field (testing ranges as well as battlefields). The main objective of this SEED project was to ascertain the suitability of specific alternative ordnance ingredients—certain explosive cyclic dinitrourea derivatives—as “self-remediating” munition or submunition fills in weapons such as BLU-97/B bomblets employed in CBU-87/B Combined Effects Munitions and potentially in many other munition systems that employ conventional nitramines (HMX or RDX) as the main explosive charge. This suitability as a self-remediating munition fill would be demonstrated by quantitative measurements of the stability of specific proposed ingredients under likely environmental conditions under which such munitions might be deployed. It was desired that such ingredients present in possible UXO would undergo adventitious degradation from environmental exposure—while remaining stable under controlled storage prior to deployment—but alternatively could be intentionally remotely and harmlessly degraded in a simply but properly designed munition configuration.

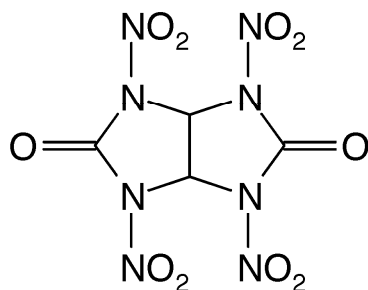
Background

Submunition fills in weapons such as BLU-97/B bomblets pose safety and/or environmental hazards if they end up as UXO due to dudding. Incomplete (low-order) detonation of fills in larger munitions that employ nitramine-based charges—such as Mark-80 series (250-lb Mark-81 to 2000-lb Mark-84) bombs and projectiles up to 155–165 mm—could also lead to environmental and safety problems as UXO. A typical submunition fill, such as PBXN-107 in the BLU-97/B, employs RDX as the main explosive charge. RDX is known to exhibit significant deleterious environmental effects on water supplies—prevalent most conspicuously near DoD’s domestic live fire training ranges¹—so EPA has issued a guideline of a limit of 2 µg/L in drinking water.² RDX also has high to moderate mobility in soil, and its natural (aerobic) biodegradation is very slow.²

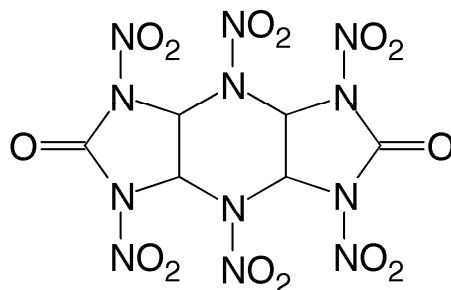
As a potential solution to persistent environmental problems posed by such ingredients in UXO, we propose consideration of a known class of explosive energetic ingredients that has received some development (predominantly in other countries) over the last couple of decades: cyclic *N,N'*-dinitrourea derivatives. Specific examples worthy of consideration for the present application are tetranitroglycoluril (TNGU or Sorguyl) and hexanitrohexaazatricyclododecanedione (HHTDD).

¹ (a) Pennington, J.C. “Distribution and Fate of Energetics on DoD Test and Training Ranges: Final Report” ERDC TR-06-13, Nov 2006; ADA458391; <http://el.erd.c.usace.army.mil/elpubs/pdf/tr06-13.pdf>; (b) Jenkins, T.F.; Hewitt, A.D.; Grant, C.L.; Thiboutot, S.; Ampleman, G.; Walsh, M.E.; Ranney, T.A.; Ramsey, C.A.; Palazzo, A.J.; Pennington, J.C. *Chemosphere* **2006**, 63, 1280.

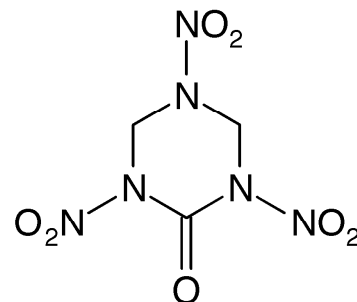
² “Cyclonite” at Hazardous Substances Data Bank: <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>



TNGU
(Sorguyl)



HHTDD



K-6
(keto-RDX)

A property these compounds have in common that has kept them from widespread adoption by most weapons systems is a property that makes them attractive in specific systems that are susceptible to causing environmental problems as UXO: they are significantly more hydrolytically reactive than simple alicyclic nitramines such as RDX. The cyclic dinitrourea tetrahydro-1,3,5-trinitro-1,3,5-triazin-2(1*H*)-one (K-6 or keto-RDX) was also tentatively considered for study in this project, but in light of its past scale-up and characterization of energetic properties at Lawrence Livermore National Laboratory³—in contrast to HHTDD and TNGU, which have received little development in this country—K-6 was withdrawn from study in this SEED project.

Because of this hydrolytic reactivity, ordnance fills that employ any of these ingredients must account for it in their formulation and processing; however, such handling is eminently feasible, as demonstrated by past early-stage development of them in France, China, and Russia. With handling problems technologically solved, these ingredients would offer attractive performance advantages, particularly in the case of HHTDD, which is recognized to be the most powerful easily accessible explosive compound,⁴ surpassing even CL-20 in explosive performance. Relevant performance parameters of the proposed dinitroureas are summarized in Table 1 in comparison to standard nitramines RDX, HMX, and CL-20.

³ Mitchell, A.R.; Pagoria, P.F.; Coon, C.L.; Jessop, E.S.; Poco, J.F.; Tarver, C.M.; Breithaupt, R.D.; Moody, G.L. *Prop. Explos. Pyrotech.* **1994**, *19*, 232.

⁴ Lu, M.-J. *Chinese J. Explos. Prop.* **2000**, *23*, 23.

Table 1. Explosive performance parameters of cyclic dinitroureas vs. nitramines

	Density ρ (g/cm ³)	Detonation pressure P_{CJ} (GPa)	Detonation velocity D (km/sec)	m.p./dec. (°C)
RDX	1.81	33.8	8.74	204
HMX	1.90	39.0	9.11	~277
CL-20	2.04	~46	~9.7	~253
TNGU	1.98–2.01 ^a	38.7 ^b	~9.20 ^c	~200 ^c
HHTDD	2.07 ^d	46.2 ^e	~9.75 ^{d,f}	215 ^g

^a Boileau, J.; Wimmer, E.; Carail, M.; Gallo, R. *Bull. Soc. Chim. France* **1986**, 465.

^b Muthurajan, H.; Sivabalan, R.; Talawar, M.B.; Asthana, S.N. *J. Hazard. Mater.* **2004**, A112, 17.

^c Boileau, J.; Emeury, J.-M.L.; Kehren, J.-P. *U.S. Patent* 4487938 (1984).

^d Hu, R.; Lu, X.; Fang, Y. *J. Energ. Mater.* **1993**, 11, 219.

^e Ju, X.-H.; Xiao, J.-J.; Xiao, H.-M. *Chinese J. Struct. Chem.* **2003**, 22, 223.

^f Zhilin, V.F.; Rudakov, G.F.; Ladonin, A.V.; Sinditskii, V.P.; Egorshv, V.Yu.; Berezin, M.V. *International Annual Conference of ICT [Proc.]* **2003**, 34, 141/1.

^g Vedachalam, M.; Ramakrishnan, V.T.; Boyer, J.H.; Dagley, I.J.; Nelson, K.A.; Adolph, H.G.; Gilardi, R.; George, C.; Flippen-Anderson, J.L. *J. Org. Chem.* **1991**, 56, 3413.

The susceptibility to hydrolysis of these ingredients was encountered early on following their initial syntheses, but it was not so great as to preclude interest in their development for possible application. TNGU was first prepared at Picatinny Arsenal in the 1950s (publicly revealed in 1974),⁵ and it was independently developed by the French starting in the 1970s.⁶ HHTDD is the newest of these ingredients, first appearing in Chinese literature in the early 1980s⁷ though not reported in Western literature until 1991,^{8,9} and it is relatively inexpensive and straightforward to prepare (Figure 1).

⁵ Minsky, I. et al. Picatinny Arsenal Memorandum Report MR-16, June 1952; cited in Fedoroff, B.T.; Sheffield, O.E. *Encyclopedia of Explosives and Related Items*, Vol. 6, 1974, p. G-117.

⁶ Boileau, J.; Emeury, J.-M.L.; Kehren, J.-P. *U.S. Patent* 4487938 (1984).

⁷ (a) Ma, M.-Y.; Lu, M.-J. *Binggong Xuebao [Acta Armamentarii]* **1980**, 3(2), 27-38; (b) Hu, R.; Fang, Y.; Lu, X. *Huozhayao* **1981**, 4, 1.

⁸ Vedachalam, M.; Ramakrishnan, V.T.; Boyer, J.H. *Heteroatom Chem.* **1991**, 2, 313.

⁹ Vedachalam, M.; Ramakrishnan, V.T.; Boyer, J.H.; Dagley, I.J.; Nelson, K.A.; Adolph, H.G.; Gilardi, R.; George, C.; Flippen-Anderson, J.L. *J. Org. Chem.* **1991**, 56, 3413.

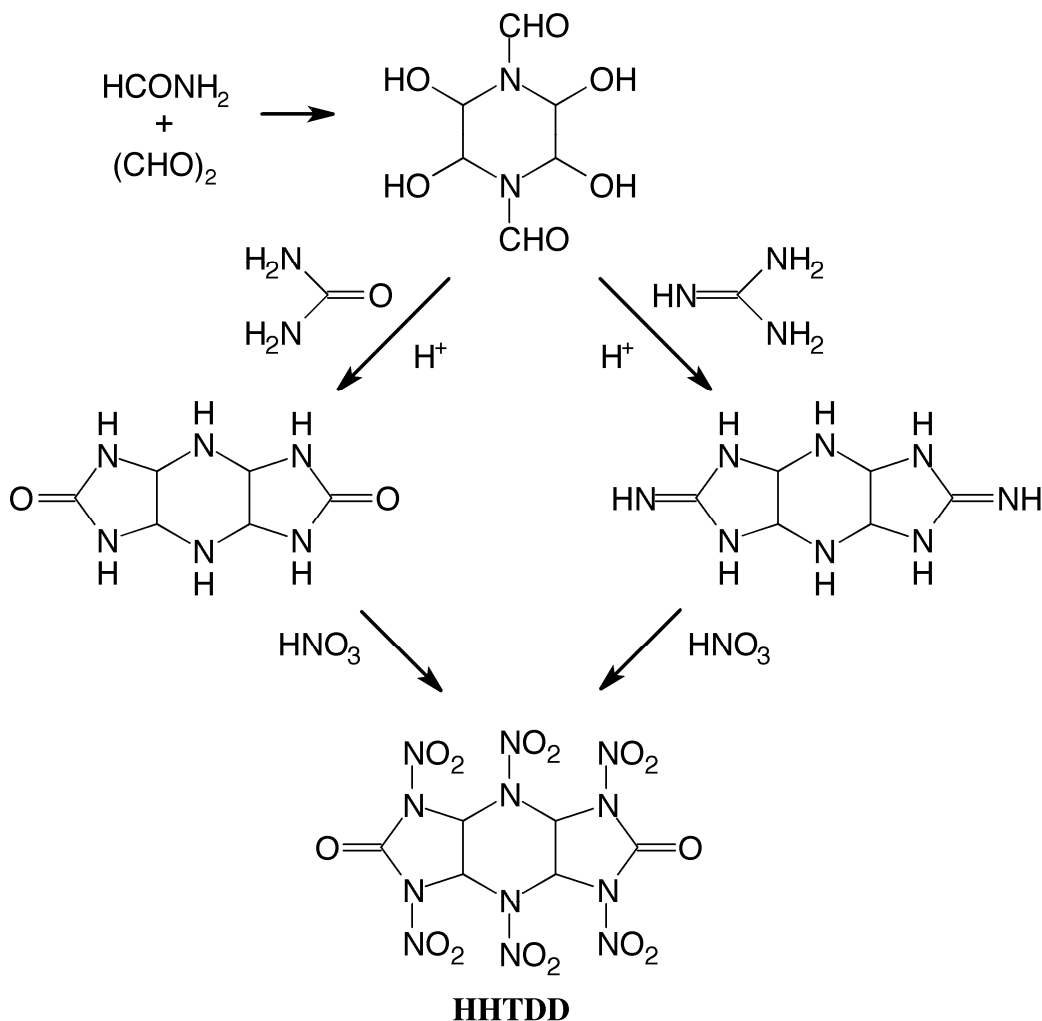


Figure 1. Synthetic routes reported to prepare HHTDD

Very few studies of hydrolysis of these ingredients—TNGU^{10,11} and HHTDD^{7,12}—have been reported, and only under relatively harsh laboratory conditions, usually intended to determine the mechanism of the chemistry involved. (Based on thermal decomposition studies, Hu et al. concluded that HHTDD has a “safe lifetime” of about 55 years at 20 °C.¹²) Such studies also showed that the ingredients do hydrolytically degrade to environmentally biodegradable small-molecule products—as shown for HHTDD in Figure 2, for example. (Glyoxal is known to be readily biodegradable and relatively benign at low concentrations.¹³) TNGU hydrolyzes via 1,1,2,2-tetrakis(nitramino)ethane to final products¹⁰ similar to those from HHTDD, as the environments around the C–C bonds are similar.

¹⁰ Peng, Z.; Wan, D. *Binggong Xuebao* **1980**, 3(3), 23.

¹¹ Hu, R.; Liang, Y.; Fang, Y.; Wang, J.; Xie, Y. *J. Therm. Anal.* **1996**, 46, 1283.

¹² Hu, R.; Lu, X.; Fang, Y. *J. Energ. Mater.* **1993**, 11, 219.

¹³ “Glyoxal” at Hazardous Substances Data Bank: <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>

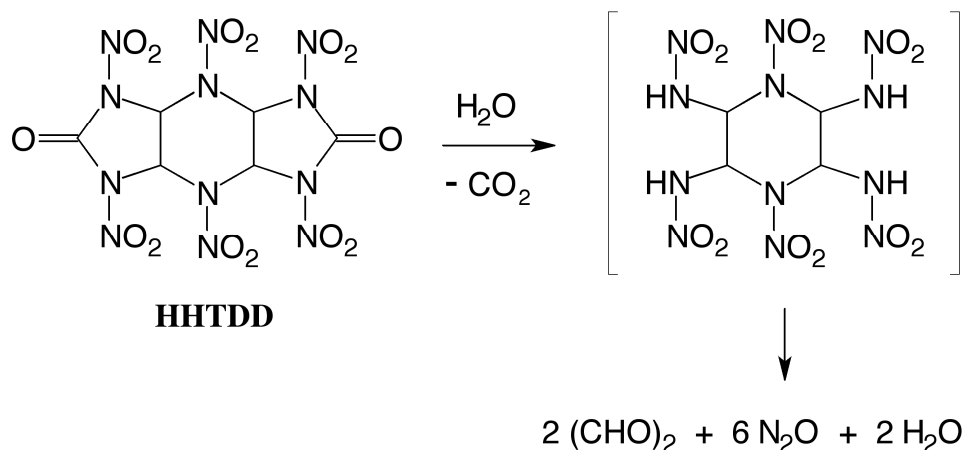


Figure 2. Suggested hydrolysis mechanism of HHTDD¹²

No studies of these dinitroureas' degradation under typical environmental conditions were found in the open literature. We therefore undertook such studies in this SEED project to demonstrate that one or more of these ingredients show(s) acceptable stability—with adequate handling precautions—for processing into munitions (generally proven in the precedent development of these materials) but also suitable reactivity with environmental elements that they would undergo sufficiently rapid “spontaneous” (environmentally adventitious) degradation as to constitute “self-remediation.” This elucidation of kinetics of degradation would also determine a possible requirement for design and incorporation into munitions hardware of a mechanism whereby the explosive fills can be alternatively degraded. Such a mechanism hypothetically could be as simple as exposing the fill to a reservoir of water—upon non-detonating impact or upon intentional remote, e.g., radio-activated control—if the munition initially survives as UXO.

Materials and Methods

TNGU¹⁰ and HHTDD were prepared according to literature procedures. We found that the preparation of HHTDD¹⁴ via the guanidine derivative dodecahydro-2,6-diimino-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine (**2**)—from the reaction of 1,4-diformyl-2,3,5,6-piperazinetetraol (**1**) with guanidine¹⁵—was preferable to the urea route (Figure 1) by giving cleaner final product via nitration (Figure 3).

¹⁴ Vedachalam, M.; Ramakrishnan, V.T.; Boyer, J.H. *Heteroatom Chem.* **1991**, 2, 313.

¹⁵ Dagley, I.J.; Flippen-Anderson, J.L. *Aust. J. Chem.* **1994**, 47, 2033.

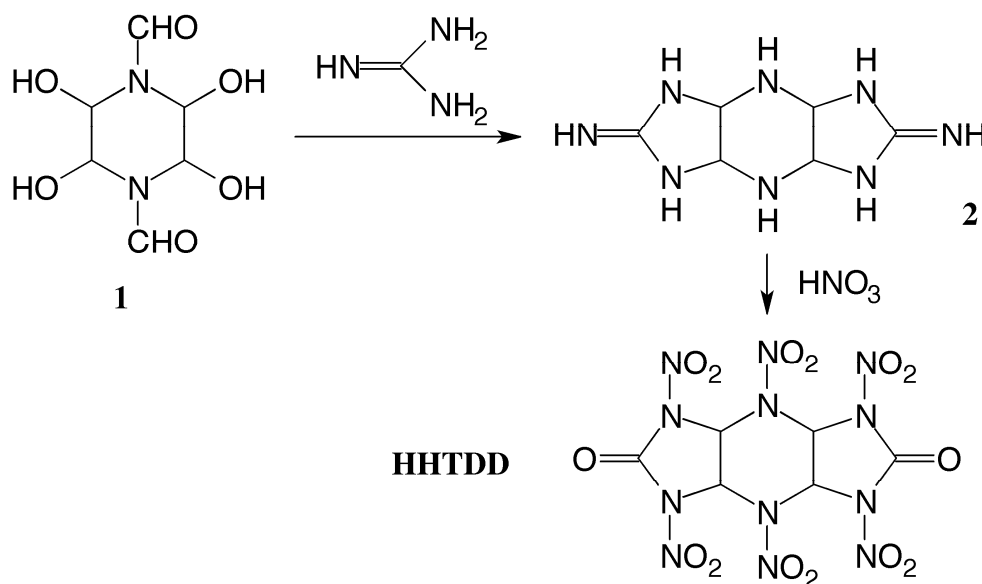


Figure 3. Chosen preparation of HHTDD¹⁴

Although past analytical procedures devised for quantification of residual energetics in soils employed high-performance liquid chromatography (HPLC) as an analytical technique,¹⁶ and we initially considered this method as well, we came to recognize in the course of method development that typical mobile phases employed in reverse-phase HPLC may interfere with accurate measurements of cyclic dinitrourea content by reaction of the water component of the mobile phase with the energetic analyte, if the cyclic dinitrourea were particularly reactive with a high concentration of water, as was suspected. (Results eventually determined in this project justified this concern.) Pure acetonitrile was attempted as a mobile phase in the course of method development, but it was discovered that this solvent did not allow adequate separation of the dinitrourea analytes from their degradation products. Therefore a new analytical method was developed based on quantitative proton nuclear magnetic resonance (¹H NMR) spectrometry.

Specifically, extraction of the energetic analyte from soil samples was performed using deuterioacetonitrile (acetonitrile-*d*₃), allowing subsequent direct analysis of the extracts by ¹H NMR. Integration of the analyte's single peak in its ¹H NMR spectrum referenced to the quintet of the residual protons in the minor content of acetonitrile-*d*₂ (CHD₂CN) as an internal standard allowed consistent quantitative measurements of relative analyte content as long as the same manufacturer's lot of CD₃CN was used throughout a kinetic run. A sample spectrum obtained by this method is shown in Figure 4. The singlet due to the protons of the bridging methine (CH) groups of HHTDD has a chemical shift of δ 7.88; the singlet from TNGU comes at δ 7.27; and the residual protons from CHD₂CN occur as a quintet centered at δ 1.94. Water when present at a low level (~1%), such as extracted from "dry" soil, occurs as a singlet at δ 2.17; at high concentrations, such as extracted from moist soil, it occurs as a broad absorption centered at about δ 2.8; its chemical shift is variable, dependent on the polarity of the solvent mixture.

¹⁶ Jenkins, T.F.; Bartolini, C.; Ranney, T.A. "Stability of CL-20, TNAZ, HMX, RDX, NG, and PETN in Moist, Unsaturated Soil" ERDC/CRREL TR-03-7, April 2003; http://www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/TR03-7.pdf

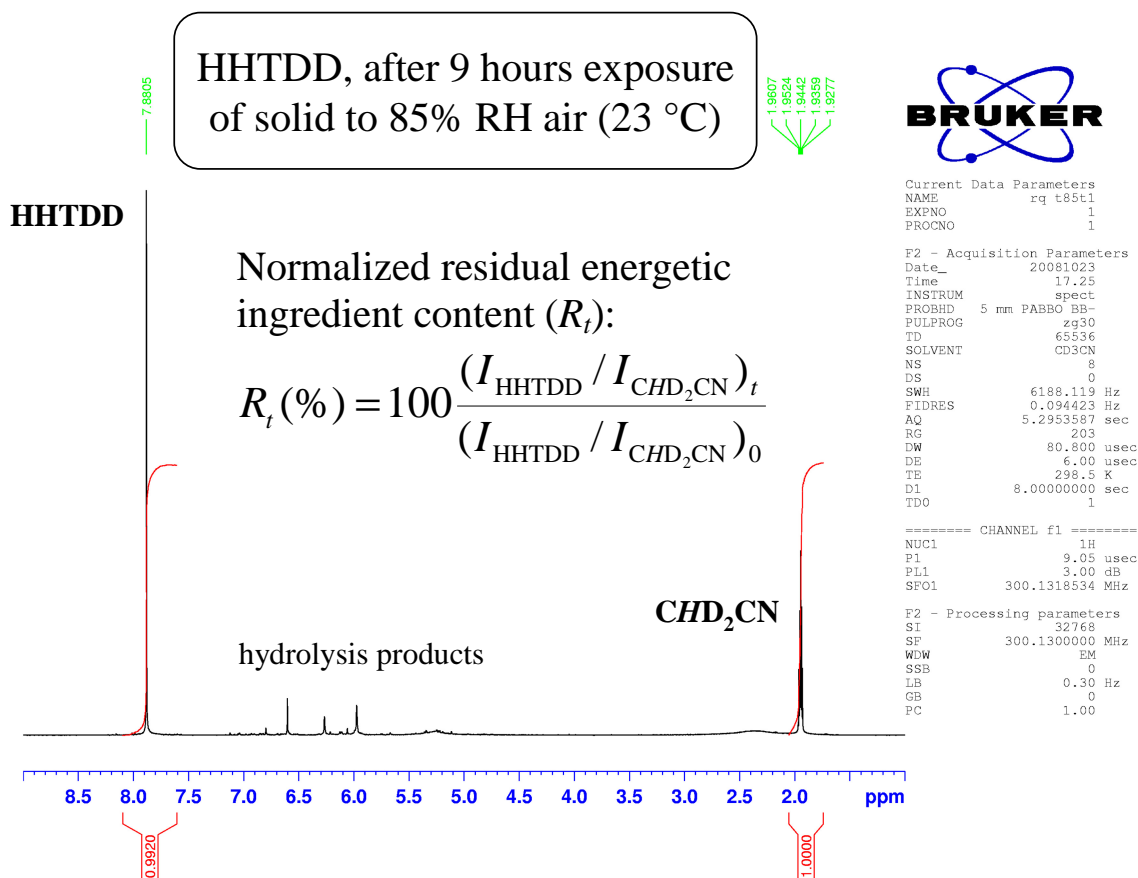


Figure 4. ^1H NMR spectrum obtained from a typical sample extract

Either a 400-MHz Bruker Avance or 300-MHz Bruker Avance II spectrometer was used to acquire ^1H NMR spectra. (Tests for consistency between the two spectrometers showed that integrations obtained from a sample were essentially identical when equivalent spectral parameters, such as pulsewidth and recycle delay, were used.) A recycle delay of 8 seconds (total recycle time of 10.9–13.3 sec) was typically employed in order to allow adequate relaxation of both components' protons for quantitative integration. (Triplicate spectra were taken of most samples in order to obtain average integrations.) In some spectra, the tails of the CHD₂CN quintet and of the singlet due to water extracted from the soil samples slightly overlapped—more likely on the 300-MHz spectrometer, especially if imperfections in the z^4 shim were present¹⁷—and in these cases, extraneous signal in overlapping tails was eliminated by deconvoluting the peaks into simple, symmetrical Lorentzian curves that fit the experimental data for a predominant proportion of their absorptions. (The deconvolution function of Bruker TopSpinTM software has been used in other quantitative resolutions of partially overlapping NMR signals.¹⁸) Then the

¹⁷ Chmurny, G.N.; Hoult, D.I. *Concepts Magn. Reson.* **1990**, 2, 131.

¹⁸ (a) Acetti, D.; Brenna, E.; Fronza, G.; Fuganti, C. *Talanta* **2008**, 76, 651. (b) Fonseca, C.; Neves, A.R.; Antunes, A.M.M.; Noronha, J.P.; Hahn-Hägerdal, B.; Santos, H.; Spencer-Martins, I. *Appl. Environ. Microbiol.* **2008**, 74, 1845.

analyte's integral was referenced to the deconvoluted CHD₂CN quintet's *proportion* of the whole H₂O + CHD₂CN integral.

Energetic analytes exposed to air were prepared as samples of ~0.014 gram weighed precisely into vials which were then stored open either in ambient (laboratory) air—whose humidity was monitored regularly and averaged $27.6 \pm 5.8\%$ relative humidity (RH), with samples protected from falling debris by loose laboratory wipes—or in a closed jar with saturated potassium chloride solution, which provides a humidity of 85% RH at an ambient temperature of 23 °C.¹⁹ Immediately prior to analysis, 0.700 mL of CD₃CN was added via syringe.

The preprocessing of soil and an extraction procedure for energetics from the soil were slightly modified from previously established methods.²⁰ The soil used in this study was “specially selected” Horizon A top soil, procured from Ward's Natural Science,²¹ which was passed through a #35 sieve (0.495-mm openings) and air-dried at room temperature. Samples of energetics in “dry” soil were prepared by mixing ~400 mg soil with ~40 mg of energetic. The samples were precisely weighed and agitated with a spatula to mix them, and the vials were exposed to ambient (laboratory) air until extraction and analysis. Samples of energetics in “moist soil” were prepared by mixing ~1.00 gram of soil, ~100 mg of energetic, and 0.250 mL of deuterium oxide (to minimize interference of a large H₂O absorption in the ¹H NMR spectrum). Energetic ingredients were extracted from soil by adding 2.00 mL CD₃CN for dry soil samples or 5.00 mL CD₃CN for moist soil samples, shaking well, sonicating the mixture for 5 min, shaking well, and sonicating for 10 seconds. After settling for 5 minutes, ~1 mL of the supernatant solution was centrifuged at 14.5k rpm for 1 minute, and the supernatant solution was used for NMR analysis. Early method development showed that longer sonication led to a measurable decrease in energetic concentration, and comparisons of immediate analyses of 5-min extracts to samples prepared without soil were essentially equivalent by quantitative NMR, indicating that extraction was complete and validating the method developed.

In order to ensure that the energetics did not undergo a rapid initial hydrolysis (to any appreciable extent) upon exposure to dilute homogeneous water in CD₃CN solution, “soil simulation” hydrolysis experiments were run with HHTDD and TNGU. The amount of CD₃CN-extractable water in the soil via our test procedure was determined by two typical extractions of TNGU-containing soil, followed by integration in triplicate spectra of the H₂O peak relative to the certified residual protium content of that lot of CD₃CN, which was 0.10% based on the reported isotopic enrichment of 99.90%D (i.e., 99.70 mol% CD₃CN + 0.30 mol% CHD₂CN). Analysis indicated that extraction of a typical 400-mg sample of soil with 2.00 mL CD₃CN introduced ~3.26 mg of water, an extractable content of 0.815 wt%. Then, separate solutions of TNGU and of HHTDD were monitored by NMR before and after adding an aliquot of water to produce a concentration of 2.4 μL H₂O/mL CD₃CN, and after sonicating a separate set of these

¹⁹ Greenspan, L. *J. Res. Nat. Bur. Stand. Sect. A* **1977**, 81A, 89.

²⁰ (a) EPA Method 8330B (Oct 2006) “Nitroaromatics, Nitramines and Nitrate Esters by High Performance Liquid Chromatography (HPLC)”; (b) ASTM Method D5143-06 (1 Nov 2006) “Standard Test Method for Analysis of Nitromaromatic and Nitramine Explosive in Soil by High Performance Liquid Chromatography.”

²¹ http://wardsci.com/product.asp_Q_pn_E_IG0004664

homogeneous solutions for 5 minutes followed by an additional 15 minutes' sonication. There was no significant change in energetic content in the water-added solutions after standing for 5 hours, nor in those after sonicating for 5 minutes, although there appeared to be a slight decrease after sonicating for 20 minutes total.

After relative residual energetic contents were determined by NMR, the results were analyzed by fitting the data to appropriate integrated rate laws that were followed by the degradation reactions (*vide infra*) using curve-fitting software that employed the Marquardt algorithm²² with robust statistical weighting. The following algorithm constants were used: “stopping tolerance” 0; “outlier tolerance” 60; “differential step” 10^{-5} ; “initial lambda” 10^6 ; “maximum lambda” 10^{50} ; “lambda factor” 10.

Results and Accomplishments

As kinetic runs under the various conditions of humidity and soil got under way, it became clear that the “dry” conditions (air and soil) were going to allow relatively long-term retention of some energetic content for both HHTDD and TNGU. In contrast, the “wetter” conditions of moist soil and of high humidity brought the experiments to completion in a very few days, so results from those experiments were available first.

Humid air experiment

The results from the high-humidity run (85% RH) were most revealing about the chemical mechanism undergone by the ingredients during hydrolysis, in that the extents of residual starting material followed logistic sigmoid patterns of decay, consistent with second-order autocatalytic reactions.²³ For HHTDD, this is consistent with the suggested hydrolysis mechanism of Figure 2, in which an ultimate product of hydrolysis (H_2O) acts as a reagent in the hydrolysis reaction. The normalized residual energetic content (R_t) data for HHTDD (Table 2) follow a classical, symmetric logistic sigmoid curve, represented by an equation of the form

$$R_t(\%) = \frac{100}{1 + e^{k(t-t_{50})}} \quad (1)$$

in which t_{50} is the time at which 50% of the original energetic content is reached. For subjective comparisons across a wide variety of conditions, t_{50} is chosen here as a figure of merit indicating the relative ease with which an energetic ingredient adventitiously hydrolyzes, i.e., “self-remediates.” For this and all kinetic runs, residual energetic content measured immediately after sample preparation (time-zero) is defined as $R_t(t=0) \equiv 100\%$.

²² Motulsky, H.; Christopoulos, A. *Fitting Models to Biological Data Using Linear and Nonlinear Regression*; GraphPad Software: San Diego, 2003; <http://www.graphpad.com/manuals/Prism4/RegressionBook.pdf>

²³ Moore, J.W.; Pearson, R.G. *Kinetics and Mechanism* (3rd ed.); Wiley: New York, 1981; Chapter 2.

Table 2. Humid air (85% RH) hydrolysis of HHTDD	
Time (days)	R_t (%)
0	100
0.375	87.407
0.937 ₅	51.424
1.458	13.679
2.354	0
4.792	0

Residual HHTDD content follows a second-order autocatalytic decay represented by

$$R_t(\%) = 100 / \{1 + \exp[3.6253(t - 0.951)]\} \quad (2)$$

with t expressed in days, shown in Figure 5 as the heliotrope curve.

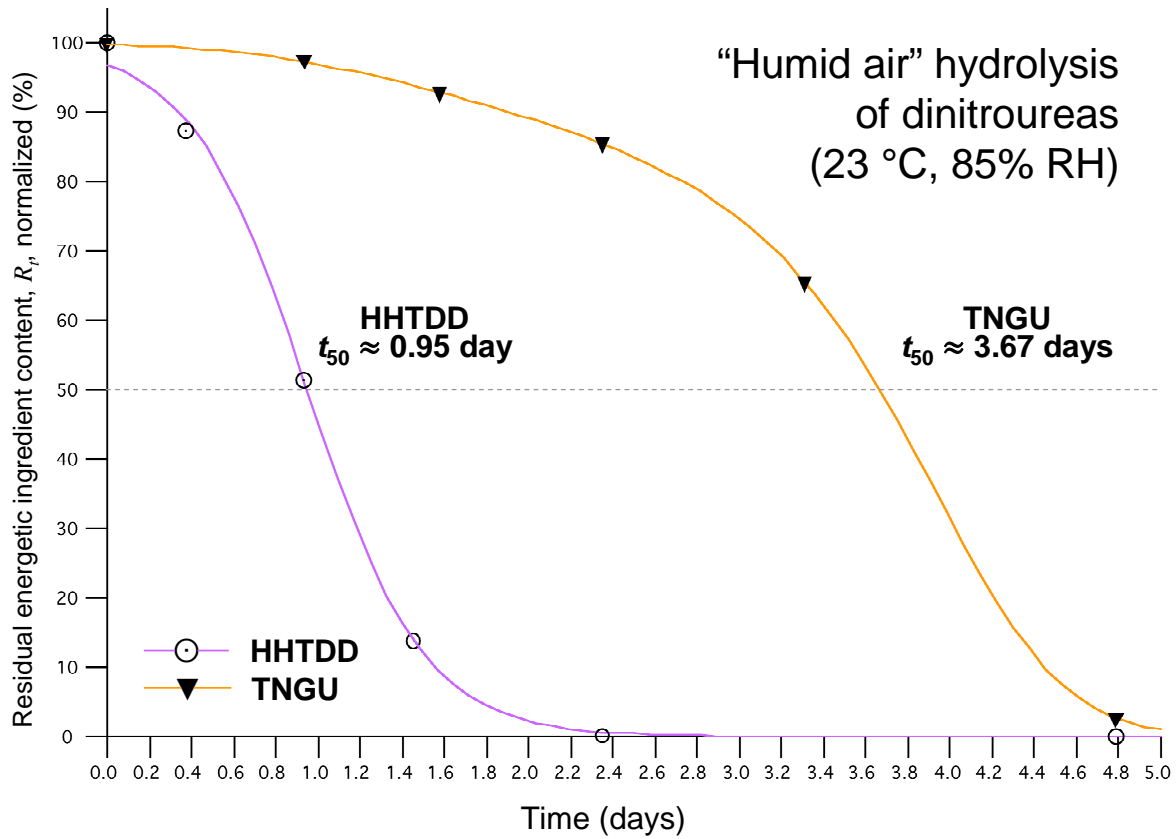


Figure 5. Degradation of HHTDD and TNGU in humid air (85% RH)

The data for TNGU (Table 3) follow a general logistic sigmoid trend, though not as symmetric as that from HHTDD.

Table 3. Humid air (85% RH) hydrolysis of TNGU	
Time (days)	R_t (%)
0	100
0.937 ₅	97.449
1.583	92.720
2.354	85.496
3.312 ₅	65.500
4.792	2.579

The data were well fit by a generalized logistic sigmoid equation (skew-growth curve) using a polynomial function of the time variable:²⁴

$$R_t(\%) = 100 / \{1 + \exp[2.0718(t-3.667) + 0.81058(t-3.667)^2 + 0.19578(t-3.667)^3]\} \quad (3)$$

with t expressed in days, shown in Figure 5 as the tangerine curve.

The figures of merit t_{50} , shown in the figure, are 0.95 day for HHTDD and 3.67 days for TNGU.

Moist soil experiment

The hydrolysis data from experiments utilizing “moist soil” (1:4 water:soil) were initially less mechanistically informative because of the relatively rapid decay of energetic content. However, with information in hand about kinetic behavior of the “humid air” experiment, it was recognizable that the energetic ingredients in moist soil were undergoing a pseudo-first-order decay²³ in the presence of a large excess of one reagent, water. Thus, the data for both HHTDD and TNGU (Table 4) were reasonably well fit by simple exponential decays (Figure 6). Because of the rapid decay that occurred in these samples, R_t was referenced to $R_t(0)$ of samples from dry soil (*vide infra*) prepared the same day, by comparing their NMR integrals corrected for weights of introduced energetic ingredient.

Table 4. Moist soil hydrolysis of HHTDD and of TNGU		
Time (days)	HHTDD R_t (%)	TNGU R_t (%)
0.062		44.383
0.075	3.605	
0.331		10.307
0.792	0	
1.086		0.375

HHTDD disappeared quite rapidly in the presence of this excess water, following a decay represented by

$$R_t(\%) = 100 \cdot \exp(-44.3041t) \quad (4)$$

(heliotrope curve) with t expressed in days, and t_{50} is estimated as ~ 0.016 day ≈ 0.38 hour.

TNGU survived somewhat longer than HHTDD, though it was 99.6% gone after 26 hours, following a decay represented by

$$R_t(\%) = 100 \cdot \exp(-9.6570t) \quad (5)$$

(tangerine curve) with t expressed in days, and t_{50} is estimated as ~ 0.072 day ≈ 1.72 hours.

²⁴ Pearl, R.; Reed, L.J. *Proc. Nat. Acad. Sci.* **1925**, *11*, 16.

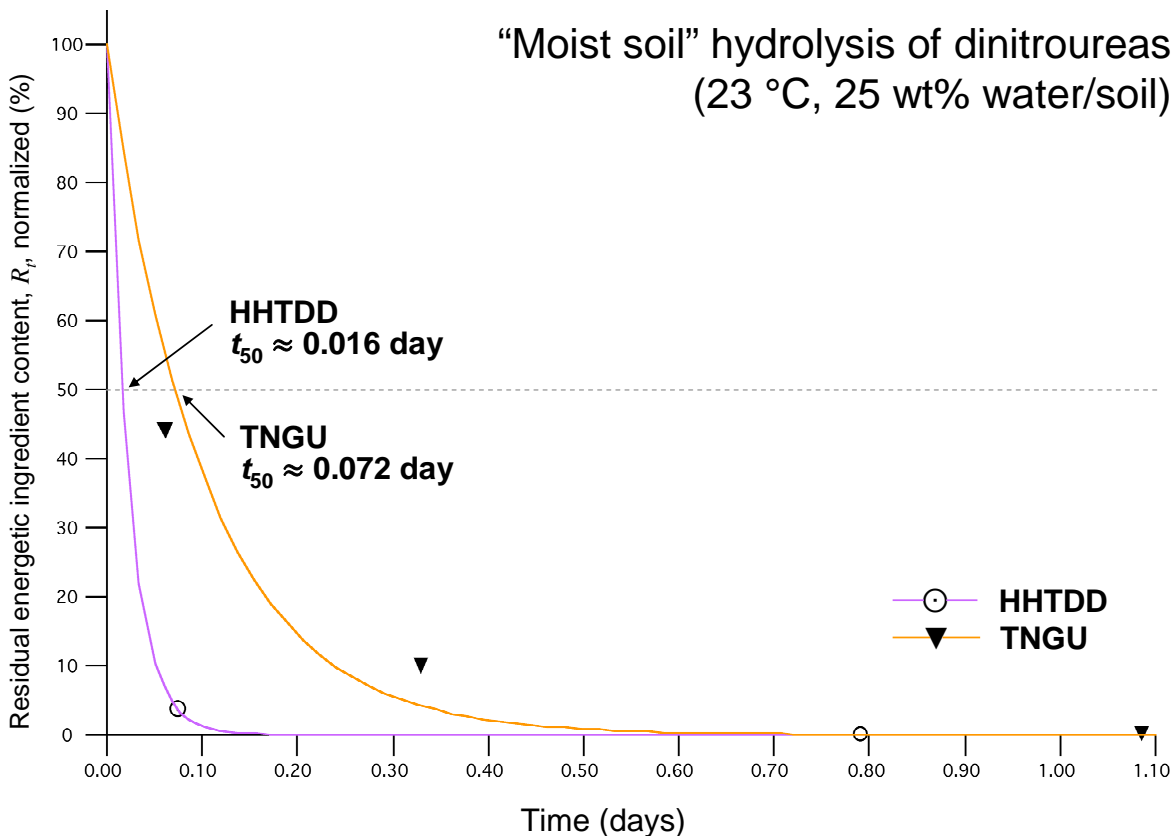


Figure 6. Degradation of HHTDD and TNGU in 1:4 water:soil

Dry air experiment

The residual energetic contents of HHTDD and of TNGU showed much slower decay without added sources of water, i.e., under ambient (laboratory) conditions of ~28% RH at 23 °C. Samples exposed only to ambient air were monitored for several months and still retained a majority of their original ingredient content. With results of the “accelerated aging” experiment offered by the hydrolysis in moist soil, it was expected that all hydrolyses of HHTDD and TNGU under conditions of relatively low water content should follow second-order autocatalytic kinetics. Thus, the normalized residual energetic content (R_t) data for HHTDD (Table 5) and for TNGU (Table 6) were reasonably well described by classical, symmetric logistic sigmoid curves (Figure 7).

Table 5. Dry air (28% RH) hydrolysis of HHTDD	
Time (days)	R_t (%)
0	100
5.858	99.277
33.800	98.174
47.035	94.759
60.975	91.615
74.778	93.573
125.808	84.492

Table 6. Dry air (28% RH) hydrolysis of TNGU	
Time (days)	R_t (%)
0	100
5.854	97.553
13.958	96.552
33.815	98.068
47.058	95.798
60.961	96.829
74.726	91.032
125.797	87.254

Residual HHTDD content follows a second-order autocatalytic decay represented by

$$R_t(\%) = 100/\{1 + \exp[0.01831(t-217)]\} \quad (6)$$

(heliotrope curve) with t expressed in days.

Residual TNGU content follows a second-order autocatalytic decay represented by

$$R_t(\%) = 100/\{1 + \exp[0.01651(t-240)]\} \quad (7)$$

(tangerine curve) with t expressed in days.

Although the figures of merit, t_{50} , appear somewhat different for the two compounds, the confidence bands of these parameters overlap even at a confidence level of only 50%: HHTDD, 217 ± 15 days; TNGU, 240 ± 19 days. Their rates of degradation in dry air are therefore essentially equivalent, and this similar behavior might reasonably be attributed to the chemical functionality that they have in common: the 1,3-dinitroimidazolidin-2-one ring, which is the molecular site that is susceptible to hydrolysis via nucleophilic attack.

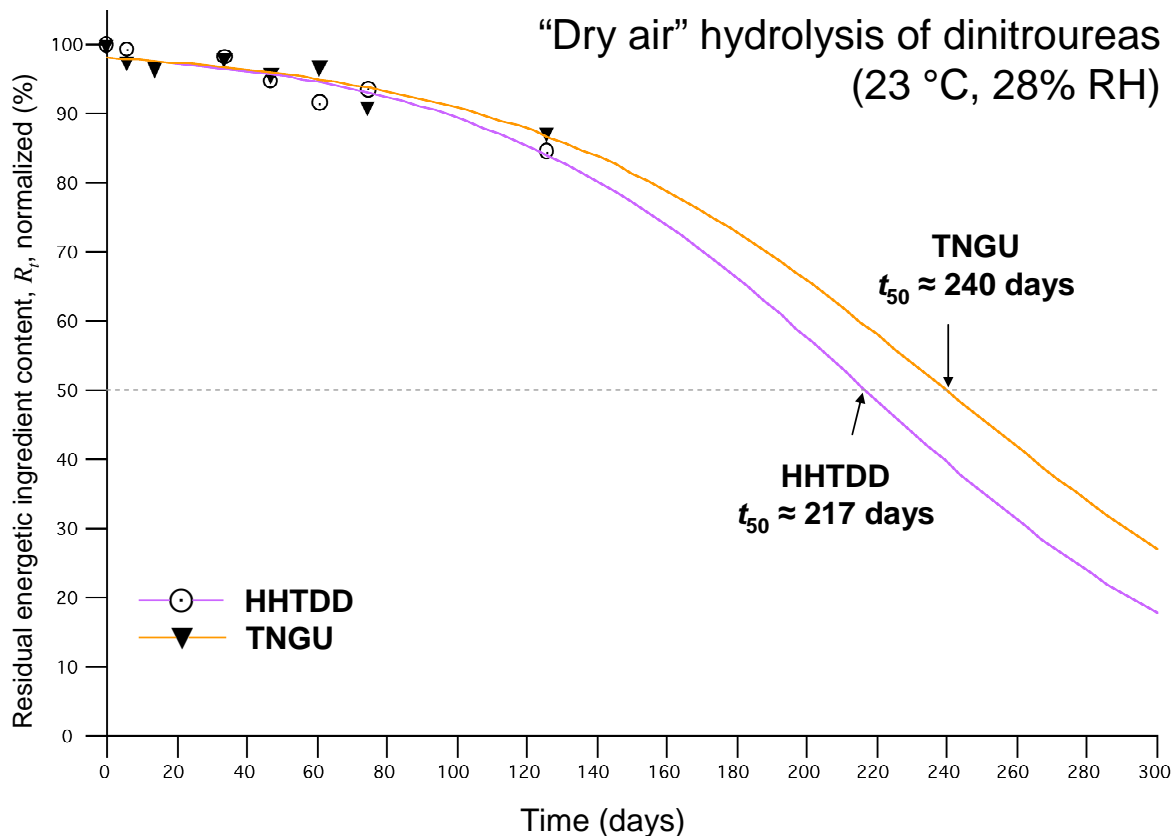


Figure 7. Degradation of HHTDD and TNGU in dry air (28% RH)

Dry soil experiment

The rates of hydrolytic decay of both HHTDD and TNGU in intimate contact with soil in dry (ambient) humidity were comparable to those in dry air without soil. The presence of heterogeneous contact with soil therefore has little effect on the rate of decay of these ingredients, and the presence of moisture is the dominant factor in determining their environmental deterioration. The normalized residual energetic content (R_t) data for HHTDD (Table 7) and for TNGU (Table 8) were reasonably well described by classical, symmetric logistic sigmoid curves (Figure 8).

Table 7. Dry soil hydrolysis of HHTDD (air@28% RH)	
Time (days)	R_t (%)
0	100
5.865	97.564
11.812	94.375
17.977	94.802
33.859	92.495
47.077	91.092
61.003	91.293
74.803	86.282
125.822	87.185

Table 8. Dry soil hydrolysis of TNGU (air@28% RH)	
Time (days)	R_t (%)
0	100
5.871	98.905
12.020	100.142
17.968	98.865
33.840	93.059
47.091	84.492
60.990	87.256
74.792	81.580
125.822	79.292

In contact with dry soil, residual HHTDD content follows a second-order autocatalytic decay represented by

$$R_t(\%) = 100 / \{1 + \exp[0.01026(t-294)]\} \quad (8)$$

(heliotrope curve) with t expressed in days.

Residual TNGU content follows a second-order autocatalytic decay represented by

$$R_t(\%) = 100 / \{1 + \exp[0.01517(t-202)]\} \quad (9)$$

(tangerine curve) with t expressed in days. The scatter of TNGU's data points is somewhat greater than its behavior in direct contact with "dry" air and of HHTDD's behavior in either system. The adjusted goodness of fit (AGFI) parameter for this nonlinear regression to TNGU's data points is 0.960, lower than those of the other fits in this study.

Although the figures of merit, t_{50} , again appear somewhat different for the two compounds, the confidence bands of these parameters overlap at a confidence level of about 65%, as shown in the figure: HHTDD, 294 ± 64 days; TNGU, 202 ± 35 days. Based on chemical mechanistic considerations and by analogy to their behavior in dry air, their rates of degradation in dry soil are probably essentially equivalent. The scatter of TNGU's data points (and even the lesser scatter of HHTDD's) might be attributable to the heterogeneous nature of the soil mix, possibly allowing for variable long-term access to atmospheric moisture among samples withdrawn and processed for analysis.

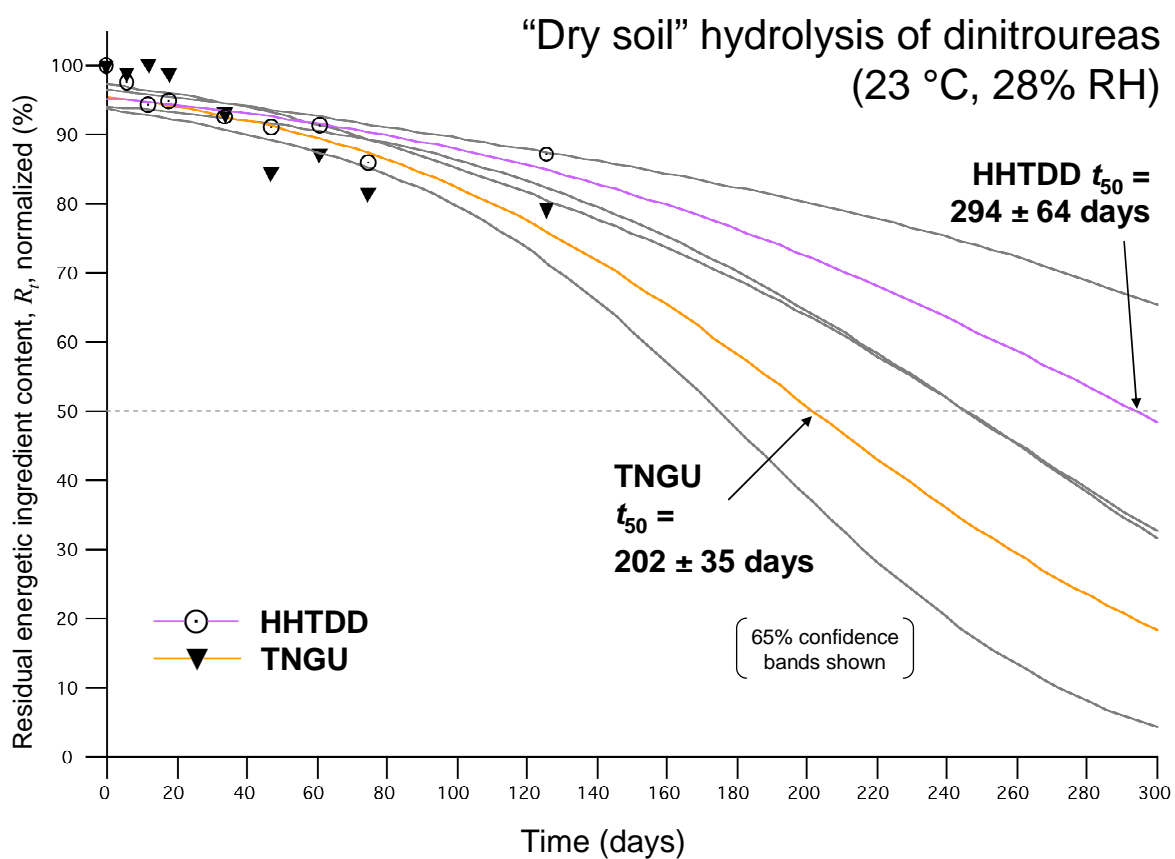


Figure 8. Degradation of HHTDD and TNGU in contact with “dry” soil (air at 28% RH)

Conclusions

The main objective of this SEED project was successfully met by demonstrating the suitability of specific alternative ordnance ingredients—certain explosive cyclic dinitrourea derivatives, HHTDD and TNGU—as “self-remediating” munition or submunition fills in weapons that would be susceptible to UXO formation. Both TNGU and HHTDD were seen to be stable enough in controlled-humidity air to be produced and processed, with no significant change occurring over a few days. In humid air, however, they degrade over a very few days, and kinetic analysis shows the hydrolysis to be autocatalytic in mechanism. In moist topsoil, both ingredients are essentially fully hydrolyzed within one day. Thus, the efficiency of environmental “self-remediation” of these ingredients is predominantly dependent on ambient humidity or access to any source of water.

Tasks 1 and 2 of the SEED project were successful in preparing the top two prioritized ingredients, TNGU and HHTDD (dinitrourea simulants of HMX and CL-20 performance, respectively), and characterizing their environmental stabilities and susceptibilities to hydrolytic degradation. Task 3, to test alternative degradation conditions, became unnecessary when it was observed that water alone acted as a suitable agent to bring about efficient remediation of the ingredients.

It is concluded, therefore, that this class of ingredients—particularly the chosen examples, HHTDD and TNGU—does offer suitable replacements for conventional nitramines in venues that are susceptible to UXO formation. (Zhilin et al.²⁵ have reviewed a variety of cyclic nitroureas, other examples of which may be suitable for simulating performance of other nitramines, such as RDX. Sikder and Sikder,²⁶ in a review including dinitroureas, note that cyclic dinitroureas incorporating six-membered rings, such as K-6, tend to be more hydrolytically stable than those based on the 1,3-dinitroimidazolidin-2-one feature, a salient characteristic in choosing prospective “self-remediating” ingredients which should be somewhat hydrolytically reactive.) These ingredients, if present in UXO, could be intentionally remotely and harmlessly degraded in a simply but properly designed munition configuration, for example, a design involving an impact-activated rupture disc or controllably environmentally degradable plug that exposes the explosive fill to environmental moisture upon deployment even in the event of dudding. If necessary in a dry environment, a subsequent wide-area water spray could accelerate hydrolysis of the UXO ingredients to complete degradation within hours.

This SEED project constituted a feasibility demonstration that certain examples of cyclic dinitroureas are potentially attractive “self-remediating” munitions ingredients. Further process development would be needed in order to develop them as replacements for current problematic formulations.

²⁵ Zhilin, V.F.; Rudakov, G.F.; Sinditskii, V.P.; Egorshv, V.Yu.; Veselova, E.V.; Ladonin, A.V.; Berezin, M.V. *Sovremennye Problemy Tekhnicheskoi Khimii, Materialy Dokladov Vserossiiskoi Nauchno-Tekhnicheskoi Konferentsii [Proceedings]*, Kazan, Russian Federation, Sept. 26–28, 2002; Volume 1, pp. 39–50.

²⁶ Sikder, A.K.; Sikder, N. *J. Hazard. Mat.* **2004**, A112, 1.

Complementary to the behavior of these main charge ingredients in self-remediating munitions, an alternative environmentally biodegradable binder might ultimately be employed in place of acrylate polymers currently used in submunitions. This design element would not be to address environmental problems posed by acrylate polymers but rather to facilitate the desired behavior of hydrolyzable explosive fills using potentially more-polar binders. Several different chemical approaches to biodegradable binders have been developed in recent years, such as ethylene glycol–adipate copolymers²⁷ or hydroxy-functionalized polybutadienes.²⁸

Following this demonstration of the suitability of the proposed ingredients as charges in new self-remediating munitions, full formulations of the submunitions should be designed in a full follow-on project and field-tested at a facility that can simulate UXO environments. A likely eventual transition opportunity is to scale up production of any newly fieldable ingredients—perhaps via ManTech or other DoD funding—ultimately transitioning to production by an energetic materials manufacturer such as ATK or Aerojet, the current manufacturer of BLU-97/B bomblets.

²⁷ Lee, B.Y.S.; Reed, R. Jr. “Degradable and Environment-Responsive Explosives” NAWCWPNS TP 8282, April 1996; <http://stinet.dtic.mil/cgi-bin/GetTRDoc?AD=ADA309058>

²⁸ Gill, R.C.; Adolph, H.G. *U.S. Patent* 6783613 (2004).

Appendix

List of Technical Publications

“Cyclic Dinitroureas as Self-Remediating Munition Charges” Robert D. Chapman, Roxanne Quintana, Lawrence C. Baldwin, Richard A. Hollins, *Partners in Environmental Technology Technical Symposium & Workshop* (Washington, DC), December 2008; <http://www.serdpestcp.org/Symposium2008/Posters/upload/T191%20-%20Chapman.pdf>.